TiO_2-CARBON HYBRID PHOTOCATALYSTS FOR THE ELIMINATION OF POLLUTANTS IN LIQUID PHASE

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Introduction

The concerns about depletion of non-renewable resources and the increasing contamination of water have contributed to the development of new methods for both energy production and pollutants removal. Photocatalytic reactions stand out for this purpose, being TiO_2 one of the most used and investigated photocatalysts. Combination of TiO_2 with activated carbon (AC) can be beneficial[1,2] because carbon can increase the photocatalyst adsorption capacity and/or decrease the recombination rate of the electron/hole photogenerated pairs[2], among other reasons. Therefore, the present study addresses the preparation of TiO_2-AC hybrid photocatalysts using sucrose as carbon precursor. The behaviour of the prepared photocatalysts is studied in two reactions in aqueous solution, of environmental interest: 1) oxidation of acetic acid (HAc), a frequent residue in different liquid effluents, to produce biogas and, 2) degradation of diuron, an herbicide commonly used in agriculture and responsible for water pollution.

Materials and Methods

An AC with spherical morphology (**Figure 1**) has been prepared from sucrose by hydrothermal synthesis followed by activation with CO_2 (80 mL/min, 5 °C/min, 800 °C, 10 h). TiO_2-AC materials have been prepared *via* sol-gel using titanium tetraisopropoxide (TTIP) and adding the prepared AC during the synthesis to obtained samples with 0, 0.5, 1, 10 wt. % AC (nominal contents). The catalysts have been submitted to a post-synthesis heat treatment (air, 350 °C, 2 h, 10 ºC/min). TiO_2 P25 (Evonik) has been used as reference.

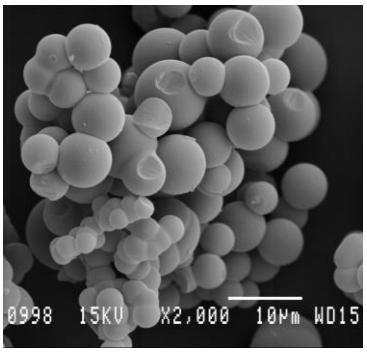

Figure 1. SEM images of the synthesized AC.

The prepared photocatalysts have been characterized by N_2 adsorption, XRD, TG analysis and SEM, and tested in the two reactions mentioned above in the following conditions:

Acetic acid oxidation: 350 mL of 1 M acetic acid, 0.35 g catalyst, room temperature, 12 h, 365 nm Hg lamp. Reaction products, mainly CH_4 and CO_2, have been quantified by mass spectrometry.

Oxidative degradation of diuron: 100 mL of a 10 mg/L diuron solution, 0.1 g catalyst, solar chamber (340 nm lamp). Diuron concentration has been determined by UV-vis spectroscopy. As diuron degradation is a pseudo first-order reaction[3], the experimental results have been fitted to a linear equation to obtain the kinetic constant.

Results and Discussion

Table 1 summarizes the characterization results. The surface area of the prepared materials tends to increase with the carbon content and is larger than that of P25. All the samples only contain anatase as crystalline phase, with crystal size (A_{Size}) around 8-9 nm. Comparing with P25, the percentage of

crystalline anatase (A_{Cryst}) in the prepared samples is a bit higher and the crystal size is clearly lower.

Figure 2 compiles the obtained photocatalytic activity data: mmoles of CH_4 and CO_2 produced in the acetic acid oxidation in 12 h and kinetic constant for diuron oxidation.

Regarding acetic acid oxidation, it can be observed that, in general, the prepared samples are more active than P25: the synthetized photocatalysts produce more CH_4 and the CH_4/CO_2 ratio is higher than in the case of the P25 commercial titania. In general, the presence of AC seems to improve the catalysts efficiency respect to that of pure TiO_2. Among the TiO_2-AC catalysts, TiO_2-AC**1** displays the highest activity. Likely, a higher AC loading might interfere with the interaction between the TiO_2 and the light.

Table 1. Textural and crystalline properties and of the prepared materials and of P25.

Sample	S_{BET} (m^2/g)	$V_{DR}(N_2)$ (cm^3/g)	A_{Size}[a] (nm)	A_{Cryst}[b] (%)
AC	491	0.25	--	--
P25	60	0.02	22	70
TiO_2	144	0.05	8	76
TiO_2-AC**0.5**	154	0.06	9	74
TiO_2-AC**1**	151	0.06	8	74
TiO_2-AC**10**	173	0.07	8	74

[a]*A_{Size}: anatase crystal size*

[b]*A_{Cryst}: percentage of crystalline anatase*

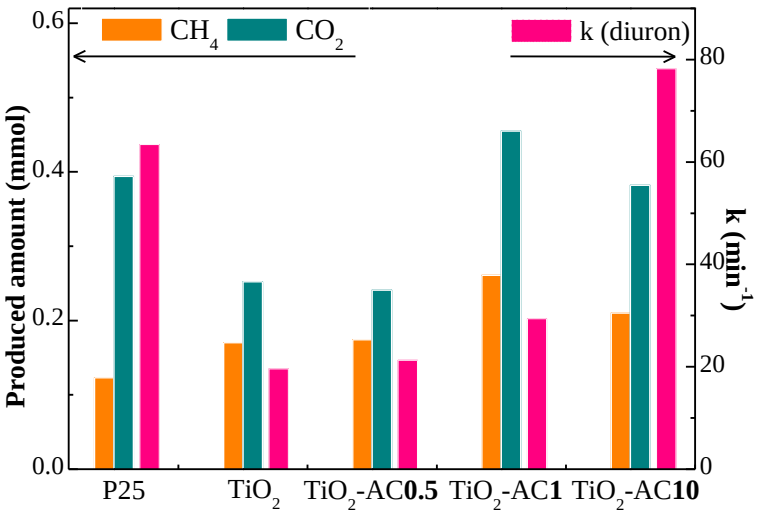

Figure 2. Amounts of CH_4 and CO_2 generated in the acetic acid oxidation (12 h) and kinetic constant values in the diuron oxidation.

In diuron degradation, the catalysts activity follows the order: TiO_2-AC**10** > P25 > TiO_2-AC**1** > TiO_2-AC**0.5** > TiO_2. The carbon-containing catalysts are more active than the prepared pure TiO_2. However, with the exception of sample TiO_2-AC**10**, they are less active than P25. The high activity of catalyst TiO_2-AC**10** is likely related with the adsorption of diuron in the AC.

Conclusions

The prepared TiO_2-AC photocatalysts are more active in the two investigated reactions than pure titania prepared in a similar way. In the acetic acid oxidation, the best results have been obtained with the catalyst containing 1 wt.% AC, while in the degradation of diuron is the catalyst with the highest carbon loading (10 wt.%) the one leading to the highest diuron removal of the catalyst (likely by a combination of adsorption and oxidation processes).

Acknowledgment

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